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H C BROWN

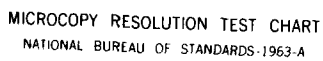
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"SUPER HYDRIDES"

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FINAL REPORT

HERBERT C. BROWN
PRINCIPAL INVESTIGATOR

1 February 1982 to 31 January 1985

U. S. ARMY RESEARCH OFFICE

GRANT NUMBER: DAAG-29-82-K-0047

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) see next page		

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20. ABSTRACT

The unusual reactivity of lithium triethylborohydride (Super Hydride) encouraged us to examine the selective reduction properties of a number of new reducing agents. Just as the replacement of hydrogen atoms in lithium borohydride (LiBH_4) with alkyl groups increases the reactivity of the reagent, substitution with alkoxy groups diminishes the reactivity. Thus, the trialkoxyborohydrides [$\text{K(RO)}_3\text{BH}$] are very mild reducing agents. A series of potassium trialkoxyborohydrides were prepared in refluxing tetrahydrofuran from the trialkoxyborane and potassium hydride. In a similar fashion, a number of monoalkyldialkoxyborohydrides [$\text{KR(OR)}_2\text{BH}$] were prepared from cyclic boronate esters and potassium hydride. We also discovered that potassium hydride reacts readily with a variety of *B*-alkoxy-9-BBN derivatives to afford the corresponding potassium dialkylalkoxyborohydrides [$\text{KR}_2\text{(OR)BH}$]. Thus we can now prepare the entire series of alkylalkoxyborohydrides: KR_3BH , $\text{KR}_2\text{(OR)BH}$, $\text{KR(OR)}_2\text{BH}$ and $\text{K(OR)}_3\text{BH}$. Although the full potentialities of these reagents are yet to be explored, preliminary studies on the reduction of cyclic ketones have shown encouraging stereoselectivities. *Originator Supplied Keywords:*

Selective reductions using potassium triisopropoxyborohydride, KIPBH, were demonstrated for aldehydes, ketones and disulfides. Other functional groups are inert to this reagent. However, KIPBH readily reduces haloboranes, producing boranes unavailable by direct hydroboration.

We have found that terminal alkynes readily produce monovinylboronates on reacting with LiBH_4 in the presence of ethyl acetate. A similar reaction is also observed with internal alkynes yielding divinylborinates. *cis*-Vinylboronates were converted into [*E*]-vinyl bromide and [*Z*]-vinyl iodide using known procedure.

The reduction of various functional groups were studied using hexylchloroborane. Compounds containing active hydrogen liberate hydrogen while ketones and aldehydes are rapidly reduced to the alcohol. Sulfoxides are

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rapidly reduced to the sulfides. Other functional groups are either unreactive or slow to react. Carboxylic acids are reduced to aldehydes with remarkable ease. Aliphatic carboxylic acids can be reduced selectively in the presence of aromatic carboxylic acids.



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INTRODUCTION

Various hydride reducing agents have evolved following the discovery by the author (with Professor Schlesinger), forty-seven years ago that diborane reduces carbonyl groups with exceptional ease. The discovery of sodium borohydride (1942) and lithium aluminum hydride (1945) have revolutionized the procedures used by synthetic organic chemists. The author's major contributions in this area, with the financial assistance from ARO, has led to the discovery of various classes of reducing agents. Consequently, a synthetic chemist can now reduce one organic functional group in the presence of the other by the proper choice of a reagent.

Electrophilic reagents, such as borane and alane, possess distinctly different reducing properties from those of nucleophilic reagents, such as sodium borohydride and lithium aluminum hydride. Investigations in this laboratory have revealed means of enhancing and diminishing electrophilic or nucleophilic properties of these reagents.

The author's discovery of hydroboration in 1956 has made available a variety of alkylboranes, which can be converted to the corresponding borohydrides. Lithium triethylborohydride (Super Hydride) is the most reactive reducing agent. Other alkylborohydrides have been prepared recently. Just as the replacement of hydrogen atoms in lithium borohydride with alkyl groups increases the reactivity of the reagent, substitution with alkoxy groups diminishes the reactivity. Thus, the trialkoxyborohydrides are very mild reducing agents.

It should be pointed out that continued research in this area will make available specific reagents which will enable us to reduce any specific functional group in the presence of any other functional group. With our

2.

increasing understanding in this area, it is hoped that we shall be in a position to design reducing agents to perform desired reductions--as specific as the enzymes designed by nature. At the same time our exploration of new compounds in this area of chemistry uncovers new high energy materials that could be of importance to defense requirements.

LIST OF PARTICIPATING PERSONS

<u>Name*</u>	<u>Period of Appointment</u>
S. Narasimhan	2/1/82 - 6/30/82
B. Nazer	2/1/82 - 5/31/83
V. Somayaji	2/1/82 - 8/31/83
J. S. Cha	8/4/82 - 7/8/84
N. M. Yoon	8/8/83 - 8/15/84
W. S. Park	5/1/84 - present
P. V. Ramachandran	6/19/84 - present
J. Chandrasekharan	10/1/84 - present
N. G. Bhat	12/1/84 - 12/31/84
S. M. Singh	12/1/84 - 12/31/84
S. Rajagopalan	12/1/84 - 12/31/84
B. Singaram	12/1/84 - 12/31/84
U. S. Racherla	12/1/84 - 12/31/84
K. S. Bhat	12/1/84 - present
R. K. Bakshi	12/1/84 - 12/31/84
J. V. N. Vara Prasad	12/1/84 - 12/31/84
M. Srebnik	12/1/84 - 12/31/84

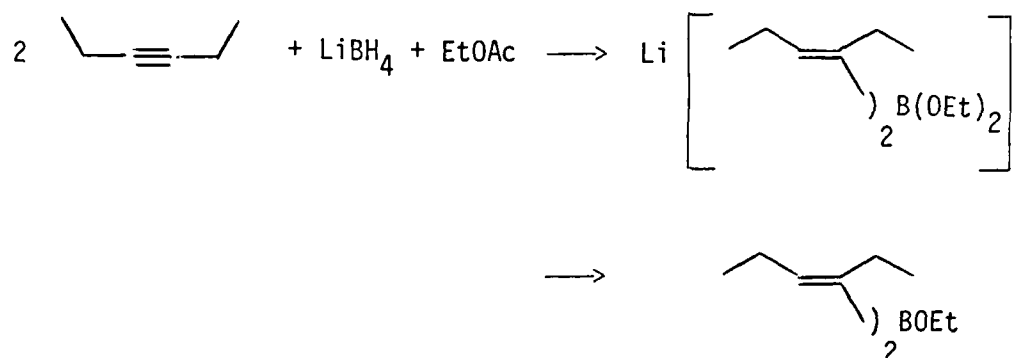
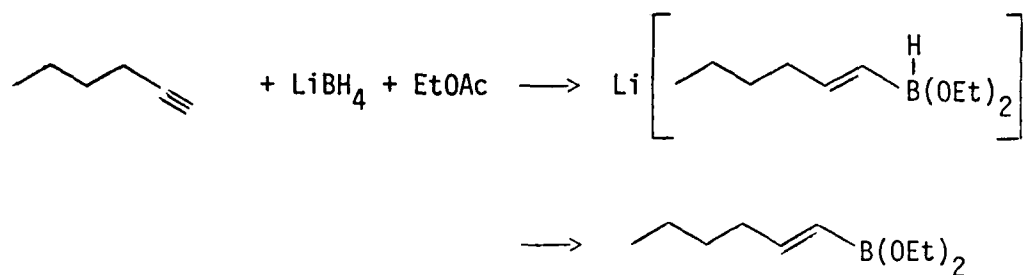
* All persons listed are Postdoctoral Research Associates.

PROBLEMS STUDIED AND THE RESULTS AND CONCLUSIONS REACHED

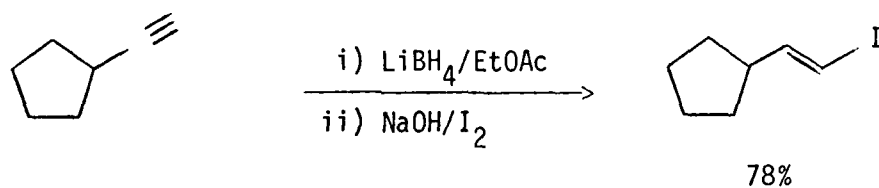
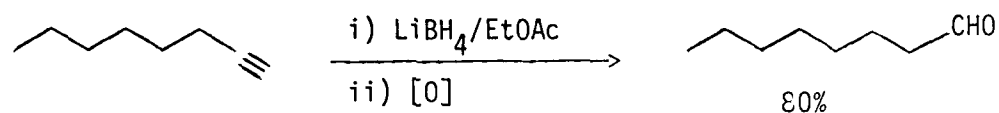
1. Controlled Hydroboration of Alkynes by Lithium Borohydride Induced by the Reduction of Carboxylic Esters

Alkynes which are normally inert to lithium borohydride are rapidly hydrobored in the presence of carboxylic esters in ether at 25°C to provide either

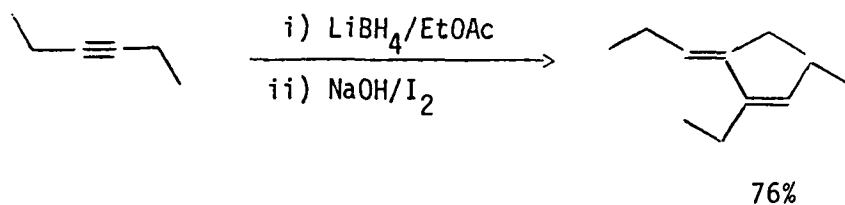
vinylboronates or divinylborinates, depending upon the structure and reactivity of the alkyne and the stoichiometry of the reagent.



The vinylboronates can be oxidized to the corresponding aldehydes or converted to the *trans*-alkenyl iodides in good yields.

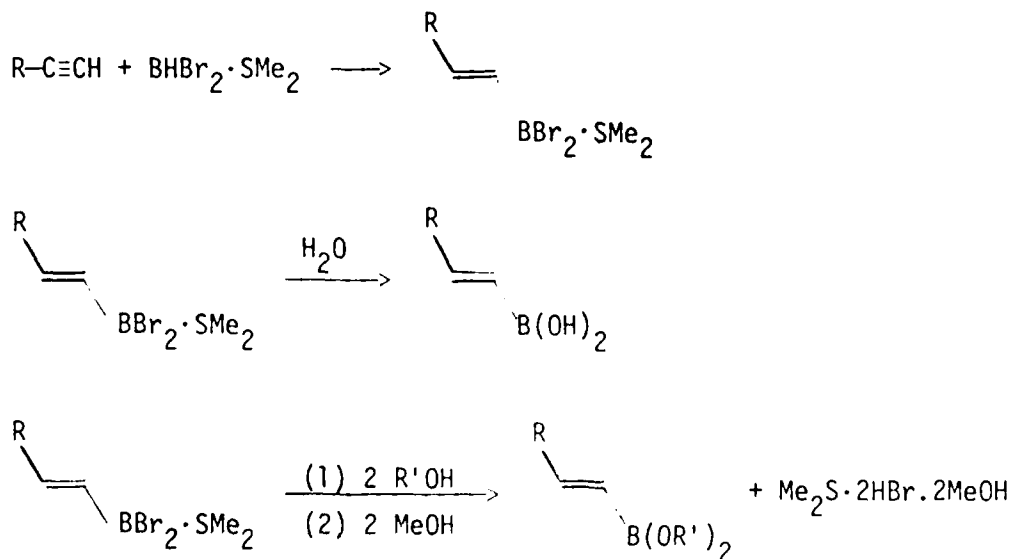


Iodide-induced migration of the divinylborinates produced the corresponding *E,Z*-dienes.

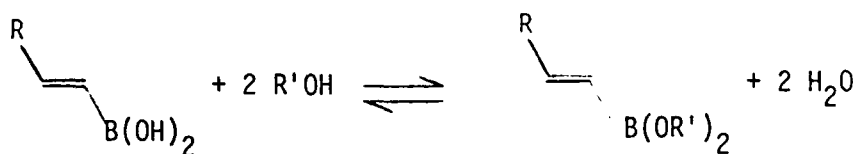


2. Alkenylboronic Acids and Esters. Synthesis of [*E*]-Vinyl Bromide and [*Z*]-Vinyl Iodides

Alkenylboronic acids and esters can also be prepared readily from the corresponding alkynes and dibromoborane-methyl sulfide complexes. Alkenyl-dibromoborane-methyl sulfide complexes obtained by the hydroboration of alkynes with $\text{BBr}_2 \cdot \text{SMe}_2$ react with water, giving the corresponding alkenylboronic acids and with alcohols and glycols to give the corresponding esters.

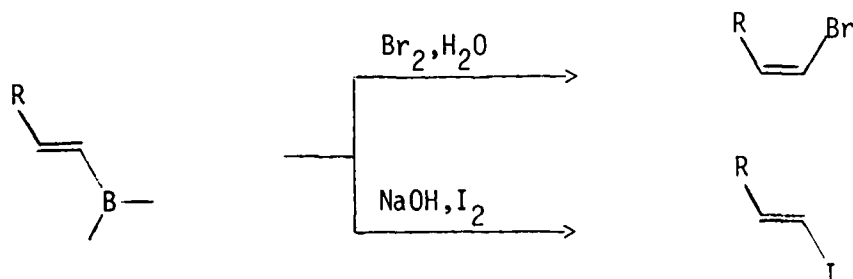


Alkenylboronic acids react with primary and secondary alcohols and glycols reversibly to form the corresponding esters.

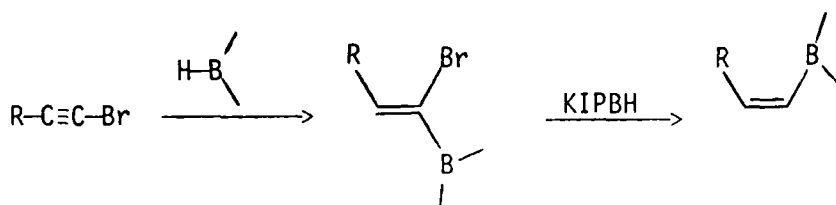


The equilibrium may be conveniently displaced in favor of ester by carrying out the reaction in pentane from which the water component separates. This procedure does away with the necessity of azeotrope distillation of a ternary mixture, extensively used previously for the esterification of boronic acids.

We previously demonstrated that treatment of *trans*-alkenylboronic acid derivatives with bromine or iodine gives the corresponding [Z]-vinyl bromides and the [E]-vinyl iodides respectively.



We have now developed a simple procedure for the synthesis of the *cis*-alkenylboronic acid derivatives by utilizing "Super Hydride" chemistry.



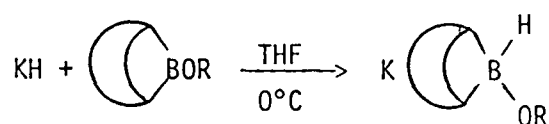
Treatment of this *cis*-alkenylboronic acid derivative with bromine or iodine gives the [E]-vinyl bromides and the [Z]-vinyl iodides in excellent yields.

3. Synthesis of Potassium 9-Alkoxy-9-boratabicyclo[3.3.1]nonanes. A New Class of Stereoselective Reducing Agents

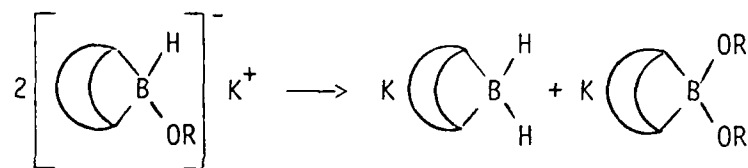
The reaction in tetrahydrofuran of potassium hydride with representative *B*-alkoxy-9-borabicyclo[3.3.1]nonanes (*B*-OR-9-BBN) containing alkoxy groups with

increasing steric requirements was examined in detail to establish the generality of this synthesis of the corresponding potassium 9-alkoxy-9-boratabicyclo[3.3.1]nonanes (K9-OR-9-BBNH) and the stereoselectivities of these new reagents for the reductions of cyclic ketones.

For *B*-methoxy-9-BBN and *B*-*n*-butoxy-9-BBN, the reactions with potassium hydride are very fast, even at 0°C. However, the products are unstable and rapidly undergo redistribution, even in the presence of excess potassium hydride.

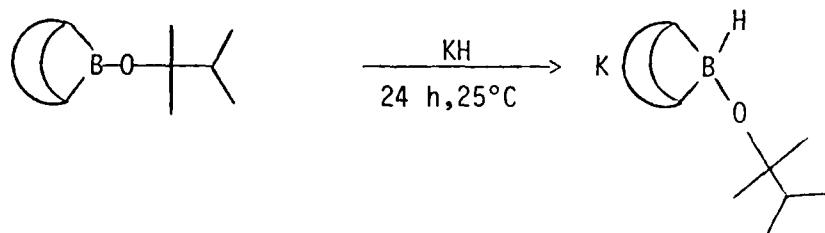


R = Me, *n*-Bu



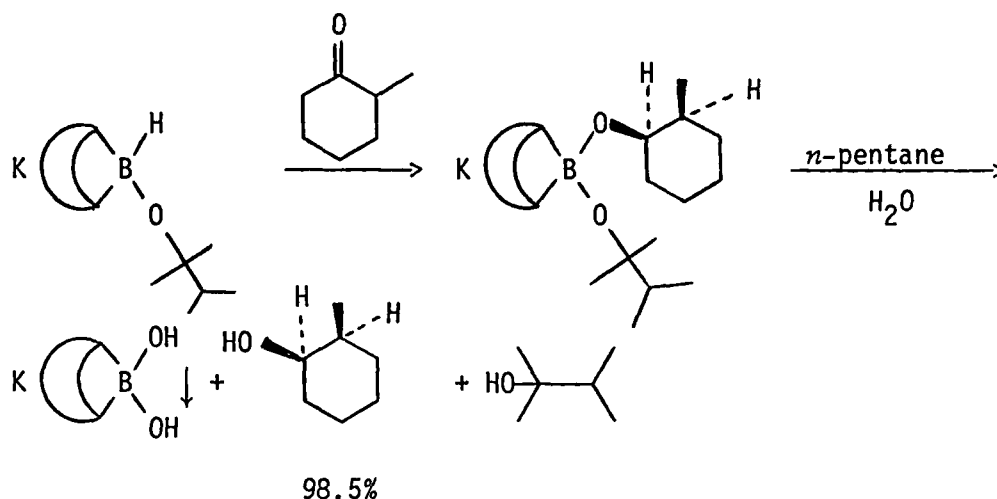
Moderately hindered alkoxy derivatives, *B*-isopropoxy-9-BBN and *B*-*sec*-butoxy-9-BBN, react somewhat slower with potassium hydride, but the products are stable to redistribution.

More hindered alkoxy derivatives, *B*-*tert*-butoxy-9-BBN and *B*-(2,3-dimethyl-2-butoxy)-9-BBN, require 24 h at 25°C to react with potassium hydride.



All reagents show high stereoselectivities generally increasing with increasing steric requirements of the alkoxy substituent. The KB-(2,3-dimethyl-

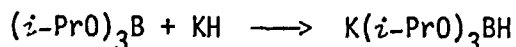
2-butoxy)-9-BBN derivative appears especially favorable with its stereo-selectivity comparable to the results previously achieved at 0°C with lithium tri-*sec*-butylborohydride. Moreover, the by-product 9-BBN derivative is easily removed as an "ate" complex, greatly simplifying the recovery of the reduction product.



4. A General Method for Preparation of Potassium Trialkoxyborohydrides.

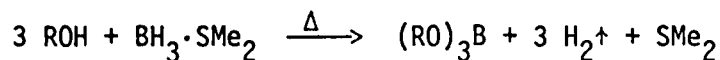
A New Class of Reducing Agents

Recently we reported an improved method for the preparation of potassium triisopropoxyborohydride (KIPBH) from triisopropoxyborane and potassium hydride.



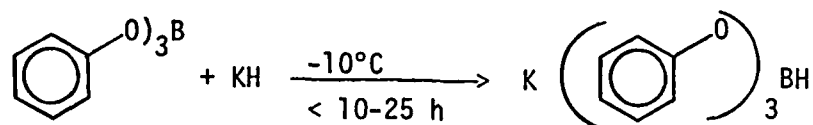
Moreover, KIPBH, thus prepared, is stable toward disproportionation at room temperature when maintained over a small excess of potassium hydride. The generality of the above synthesis of trialkoxyborohydride was examined with several additional trialkoxyboranes of varying steric requirements.

Trialkoxyboranes were prepared from the corresponding alcohols and borane-methyl sulfide complex.



The reaction of trimethoxy- and triethoxyborane with potassium hydride proceeded readily at 25°C, but the products could not be stabilized over excess potassium hydride.

Triphenoxyborane reacted readily, even at -10°C, and stabilization was achieved.



Tri-*sec*-butoxyborane and tricyclopentoxyborane required refluxing in THF for 12-24 h and the products were stabilized over potassium hydride. The reaction of tri-*tert*-butoxyborane required several days for completion. The product was quite stable toward disproportionation without excess potassium hydride.

The stereoselectivities of these reagents in the reduction of representative cyclic ketones were examined. The stereoselectivities varied in an erratic manner with the steric requirements of the alkoxy group and did not approach the stereoselectivities previously achieved with lithium tri-*sec*-butylborohydride and lithium trisiamylborohydride.

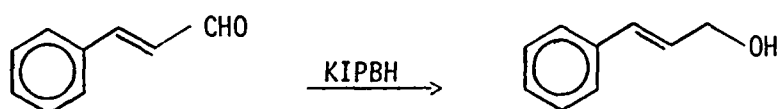
5. Potassium Triisopropoxyborohydride as a Selective Reducing Agent in Organic Synthesis. Selective Reduction of Disulfides to Thiols

Potassium triisopropoxyborohydride is a mild reducing agent. This is unexpected because hydride transfer should be very easy from a weak Lewis acid, such as (*i*-PrO)₃B, weakened by back-bonding. It seems that back-bonding does not play an important role in the transition state so that inductive effect of the isopropoxy group predominates. Because a full investigation of the

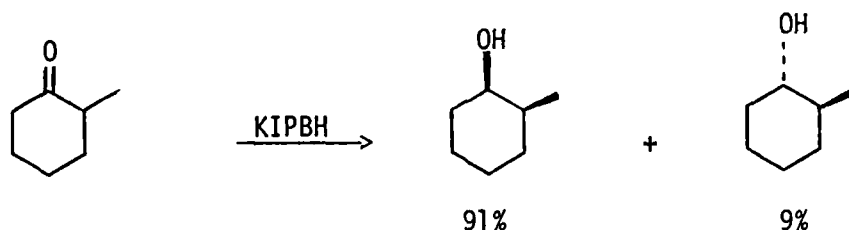
reagent was not available, we undertook to study the reaction of pure potassium triisopropoxyborohydride with our 56 compounds containing representative functional groups.

Primary, secondary and tertiary alcohols evolve hydrogen partially, even after a long period of time. Phenols also generate partial hydrogen, and the reactions of those amines and thiols studied with the reagent are very slow.

Aldehydes and ketones are reduced rapidly and quantitatively to give the corresponding alcohols. Cinnamaldehyde is rapidly reduced to cinnamyl alcohol.

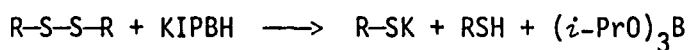


Unlike sodium and potassium borohydrides, KIPBH is very stereoselective. 2-Methylcyclohexanone can be reduced stereoselectively to *cis*-2-methylcyclohexanol.

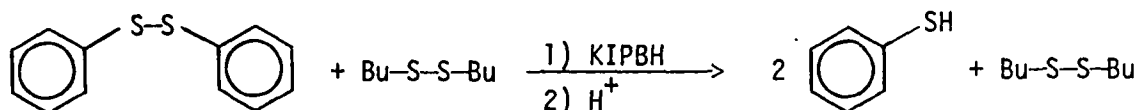


Carboxylic acids liberate hydrogen only partially and further reduction is very slow. Esters and epoxides are inert toward this reagent. Phthalide and γ -butyrolactone are reduced only slowly. Tertiary amides and nitriles are inert toward the reagent.

It reduces organic disulfides readily to the corresponding thiols.

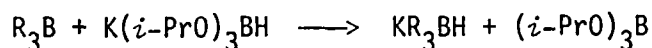
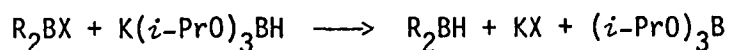


Moreover, it selectively reduces aromatic disulfides in the presence of aliphatic disulfides.

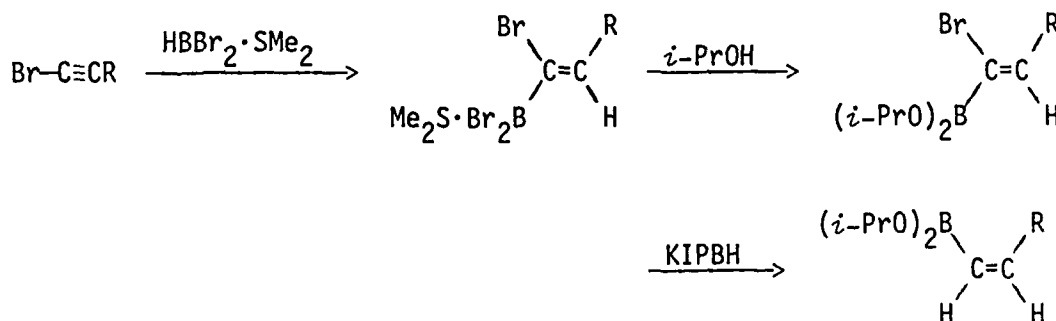


Consequently, it is now possible to reduce selectively disulfides in the presence of most other functional groups.

KIPBH readily transfers hydride to dialkylhaloboranes or trialkylboranes to produce the corresponding dialkylboranes and trialkylborohydrides respectively.



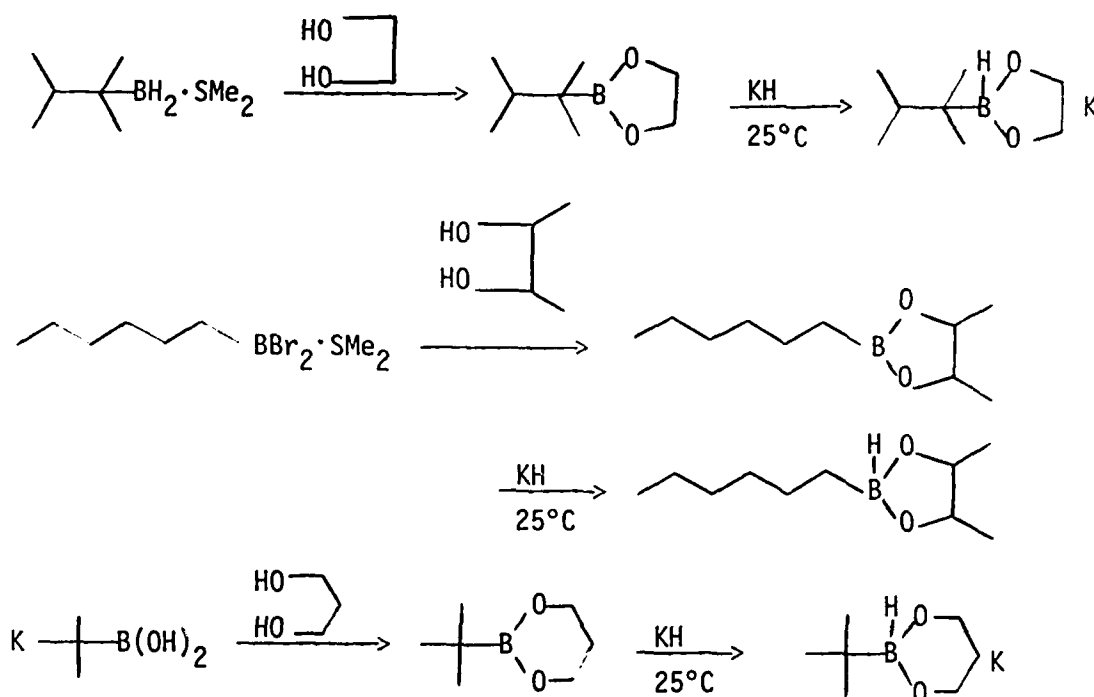
It also provides a valuable procedure for the synthesis of *cis*-vinylboronic esters.



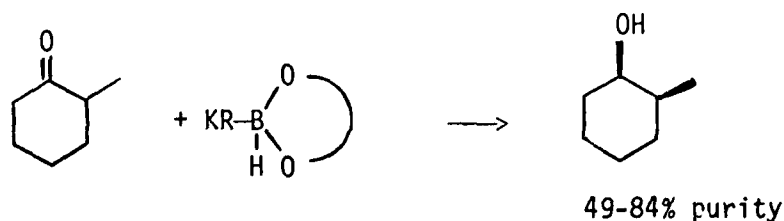
The reducing properties of KIPBH are now characterized. The reagent is a very mild reducing agent. With the exception of aldehydes, ketones and disulfides most functional groups studied were inert toward KIPBH.

6. Synthesis of Potassium Monoalkyldialkoxyborohydrides

We have discovered that the acyclic boronic esters react readily with potassium hydride, but the products are very unstable and undergo rapid disproportionation. However, the cyclic boronic esters form stable borohydrides.

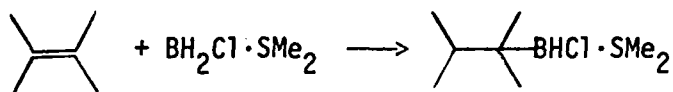


When the highly hindered pinacol ester is used, the formation of the borohydride is prevented even in refluxing THF. These monoalkyldialkoxyborohydrides reduce 2-methylcyclohexanone quantitatively, forming the less stable *cis*-isomer in 49-84% isomeric purity.



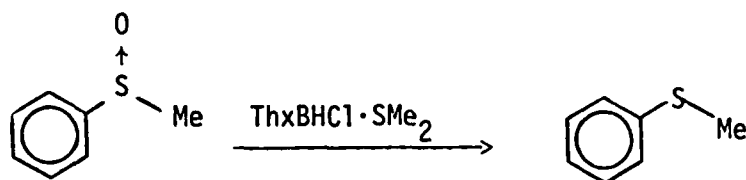
7. Selective Reductions Using Thexylchloroborane Methyl Sulfide

Thexylchloroborane methyl sulfide is readily prepared from monochloroborane methyl sulfide and 2,3-dimethyl-2-butene.



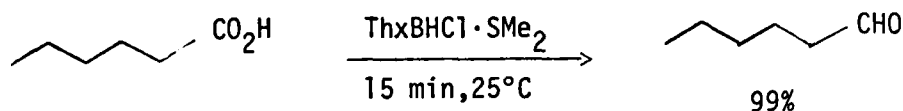
This reagent offers considerable promise as a selective reducing agent. Various classes of compounds were treated with excess reagent in methylene chloride at 0°C. Alcohols and thiols liberate hydrogen rapidly and quantitatively. Aldehydes and ketones are reduced rapidly and quantitatively to the corresponding alcohols.

Acid chlorides and acid anhydrides react only slowly with the reagent and esters do not undergo reduction under the standard conditions. Pyridine forms an addition compound, but does not undergo reduction. On the other hand, sulfoxides are rapidly reduced to the corresponding sulfides.



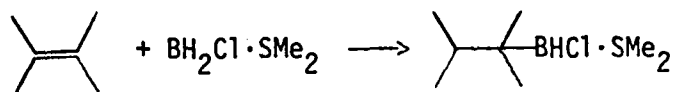
Consequently, this reagent reveals interesting differences from either borane or other borane derivatives, such as disiamylborane or 9-BBN.

In the course of this study, we also observed that this reagent reduced acyclic and alicyclic carboxylic acids to the corresponding aldehydes in high yields in approximately 15 min at 25°C.



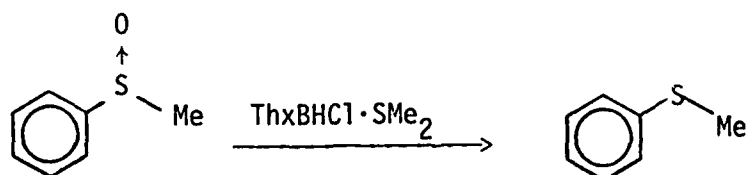
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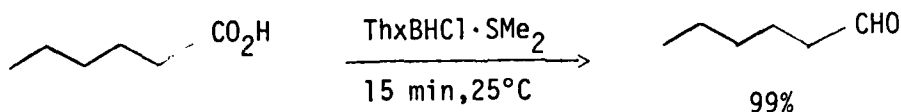
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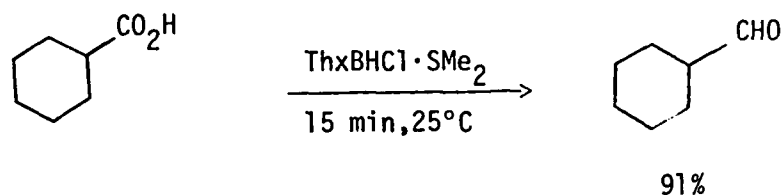
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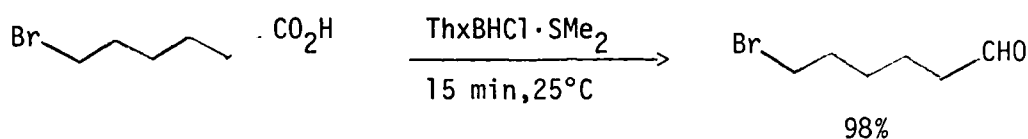
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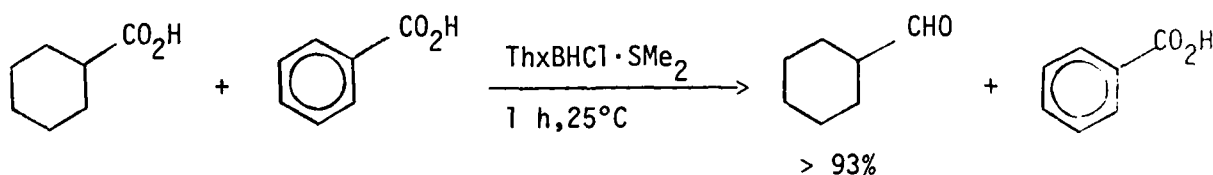




Derivatives are readily accommodated. Thus, 6-bromohexanoic acid is readily converted to 6-bromohexanaldehyde.



The reduction of aromatic acids with thexylchloroborane is much more sluggish. The reaction requires 24 h and yields are significantly lower and vary with the substituent. The remarkable difference in rates in the reduction by thexylchloroborane of aliphatic and aromatic carboxylic acids suggests the possibility of achieving the selective reduction of aliphatic carboxylic acids in the presence of aromatic carboxylic acids. Indeed, thexylchloroborane reduces cyclohexane carboxylic acid selectively in the presence of benzoic acid.



LIST OF PUBLICATIONS

This is in continuation of the list submitted with the last Final Report (Grant DAAG-29-79-C-0027 covering the period 2/1/79 - 1/31/82). Twenty-five reprints of each of the publications have been sent along with the Semi-Annual Reports.

1. New Powerful Catalysts for the Reduction of Esters by Lithium Borohydride
H. C. Brown and S. Narasimhan
J. Org. Chem., 47, 1604 (1982)
2. Controlled Hydroboration of Alkenes by Lithium Borohydride Induced by the Reduction of Carboxylic Esters
H. C. Brown and S. Narasimhan
Organometallics, 1, 762 (1982)
3. Selective Reductions. 29. A Simple Technique to Achieve an Enhanced Rate of Reduction of Representative Organic Compounds by Borane-Dimethyl Sulfide
H. C. Brown, Y. M. Choi and S. Narasimhan
J. Org. Chem. 47, 3153 (1982)
4. Addition Compounds of Alkali Metal Hydrides. 22. Convenient Procedures for the Preparation of Lithium Borohydride from Sodium Borohydride and Borane-Dimethyl Sulfide in Simple Ether Solvents
H. C. Brown, Y. M. Choi and S. Narasimhan
Inorg. Chem. 21, 3657 (1982)
5. Selective Reductions. 30. Effect of Cation and Solvent on the Reactivity of Saline Borohydrides for Reduction of Carboxylic Esters. Improved Procedures for the Conversion of Esters to Alcohols by Metal Borohydrides
H. C. Brown, S. Narasimhan and Y. M. Choi
J. Org. Chem. 47, 4702 (1982)
6. Addition Compounds of Alkali Metal Hydrides. 23. Preparation of Potassium Triisopropoxyborohydride in Improved Purity
H. C. Brown, B. Nazer and J. A. Sikorski
Organometallics, 2, 634 (1983)
7. Selective Reductions. 31. Lithium Triethylborohydride as an Exceptionally Powerful Nucleophile. A New and Remarkably Rapid Methodology for the Hydrogenolysis of Alkyl Halides Under Mild Conditions
S. Krishnamurthy and H. C. Brown
J. Org. Chem., 48, 3085 (1983)
8. Selective Reductions. 32. Structural Effects on the Reduction of Epoxides by Lithium Triethylborohydride. A Kinetic Study
H. C. Brown, S. Narasimhan and V. Somayaji
J. Org. Chem., 48, 3091 (1983)

9. Organoboranes. 30. Convenient Procedures for the Synthesis of Alkyl- and Alkenylboronic Acids and Esters
H. C. Brown, N. G. Bhat and V. Somayaji
Organometallics, 2, 1311 (1983)
10. Selective Reductions. 33. Potassium Triisopropoxyborohydride as a Selective Reducing Agent in Organic Synthesis. Reaction with Selected Organic Compounds Containing Representative Functional Groups
H. C. Brown, J. S. Cha, B. Nazer, S. C. Kim, S. Krishnamurthy and C. A. Brown
J. Org. Chem., 49, 885 (1984)
11. A New, Highly Stereoselective Reducing Agent, Potassium 9-(2,3-Dimethyl-2-butoxy)-9-boratabicyclo[3.3.1]nonane
H. C. Brown, J. S. Cha and B. Nazer
J. Org. Chem., 49, 2073 (1984)
12. Selective Reduction of Disulfides to Thiols with Potassium Triisopropoxyborohydride
H. C. Brown, B. Nazer and J. S. Cha
Synthesis, 498 (1984)
13. Selective Reductions. 36. Reaction of Lithium 9-Boratabicyclo[3.3.1]nonane with Selected Organic Compounds Containing Representative Functional Groups
H. C. Brown, C. P. Mathew, C. Pyun, J. C. Son and N. M. Yoon
J. Org. Chem., 49, 3091 (1984)
14. Molecular Addition Compounds. 9. Effect of Structure on the Reactivities of Representative Borane-Amine Complexes in Typical Reactions Such as Hydrolysis, Hydroboration and Reduction
H. C. Brown and L. T. Murray
Inorg. Chem., 23, 2746 (1984)
15. Addition Compounds of Alkali Metal Hydrides. 24. A General Method for Preparation of Potassium Trialkoxyborohydrides. A New Class of Reducing Agents
H. C. Brown, J. S. Cha and B. Nazer
Inorg. Chem., 23, 2929 (1984)
16. Selective Reductions. 35. Reaction of Representative Organic Functional Groups with Lithium Borohydride in the Presence of *B*-Methoxy-9-boratabicyclo[3.3.1]nonane. A Simple, Convenient Procedure for the Catalyzed Selective Reduction of Esters
H. C. Brown and S. Narasimhan
J. Org. Chem., 49, 3891 (1984)
17. Convenient Procedure for the Synthesis of [*E*]-1-Bromo-1-alkenes and [*Z*]-1-Iodo-1-alkenes
H. C. Brown and V. Somayaji
Synthesis, 919 (1984)

18. An Exceptionally Facile Reduction of Acyclic and Alicyclic Carboxylic Acids to Aldehydes by Thexylchloroborane-Dimethyl Sulfide
H. C. Brown, J. S. Cha, B. Nazer and N. M. Yoon
J. Am. Chem. Soc., 106, 8001 (1984)
19. Hydroboration. 69. Hydroboration Characteristics of Lithium Borohydride/Ethyl Acetate in Ethyl Ether. A New System for Controlled Hydroboration of Alkenes and Alkynes
H. C. Brown, V. Somayaji and S. Narasimhan
J. Org. Chem., 49, 4822 (1984)

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